

the dissolving reaction of CaCO_3 1 gram in 8.3 Mol acetic acid (Buffer solution $0.03\text{M C}_6\text{H}_8\text{O}_7 \cdot \text{H}_2\text{O}$, $0.1\text{M Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$) 100c.c. . For comparison, 6 kinds of CaCO_3 ($0.04\mu \sim 50\mu$ in dia.) were also examined by other methods, such as electron microscope, sedimentation method, absorption method, microscope and sieving method and our method, was found very accurate.

19. Studies on the Reactions of Hydrogenation by the Method of Thermal Analysis.

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The hydrogenation of fatty acids has been studied by many investigators since 1897, but there exist only few reports on the kinetics and the heat of the reaction. So we studied kinetically the hydrogenation of oleic acid as an example of the simplest fatty acid by the method of thermal analysis of reaction velocity in liquid phase. (This report, 17 (1949) 31, Rev. Phy. Chem. Japan 11, (1937) 439, 13 (1939) 24, 20 (1946) 35) In the reaction vessel (a Dewar vessel) immersed in thermostat (oil bath), preheated hydrogen gas was passed into the oleic acid mixed with Raney catalysts, and the rise of temperature was recorded with time. The temperature of the reaction was 80°C , 100°C and 120°C , respectively, oleic acid 29.9 or 49.6g, catalysts 0.3~1.2g, flow rate of hydrogen 0.2, 0.4 and 0.6 l/min. and the reaction time 60 min. . It was found that the hydrogenation of oleic acid was the first order reaction and the velocity constants were small. Also the rate of reaction was proportional to the quantity of catalysts and the flow rate of hydrogen.

$$\text{So } \frac{dx}{dt} = k \cdot [\text{quantity of catalysts}] \times [\text{flow rate of hydrogen}] \\ \times (\text{concentration of oleic acid})$$

And the value of activation energy was 8.3 Kcal, calculated from Arrhenius equation. The relation between the heat quantity emitted in a given time and the difference of the iodine value of oleic acid in beginning and at the end of reaction is linear and from this the heat of hydrogenation of oleic acid was evaluated as 37.2 Kcal/mol as the average value of 15 experiments.

As mentioned above we obtained the good results in application of the thermal analysis to the high temperature reaction in the liquid phase.